

CIT 220-3/TR-12
c. 36

AD No. 21013
ASTIA FILE COPY

PROPERTY OF R.D.
TECHNICAL LIBRARY

Copy No. 36

CALIFORNIA INSTITUTE OF TECHNOLOGY
GUGGENHEIM JET PROPULSION CENTER
Pasadena, California

THE f-VALUES OF SPECTRAL LINES

BELONGING TO THE

$^2\Sigma - ^2\Pi$ TRANSITION OF OH

by P. J. Dyne

Technical Report No. 12
Contract No. Nonr-220(03), NR 015 210
Submitted by: S. S. Penner

November 1953

THE f-VALUES OF SPECTRAL LINES BELONGING TO THE
 $^2\Sigma - ^2\Pi$ TRANSITION OF OH *

P. J. Dyne[†]

Guggenheim Jet Propulsion Center
and
Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, Pasadena, California.

A redetermination has been made of the f-values of spectral lines belonging to the $^2\Sigma - ^2\Pi$ transition of OH which were previously measured by Oldenberg and Rieke. A lower limit to the f-value has been obtained which is about one half as large as the value of Oldenberg and Rieke. A critical analysis of the experimental data shows that the effects of lack of resolving power in both intensity determinations are serious and not fully understood.

I. Introduction

During the years 1934-38 Oldenberg and his colleagues¹ made a detailed study of the kinetic behavior of OH in various systems using its ultra-violet absorption spectrum as a method of detection and of measuring its relative concentration. The absolute intensity of this $^2\Sigma - ^2\Pi$ transition of OH was first measured with high resolving power by Oldenberg and Rieke² [hereafter referred

* Financial support for this work was provided by the Office of Naval Research under Contract Nonr-220(03), NR 015 210 and by the Daniel and Florence Guggenheim Jet Propulsion Center. The experimental work was carried out in the Gates and Crellin Laboratories of Chemistry

[†] Post-Doctorate Research Fellow in Jet Propulsion.

- ¹ a) O. Oldenberg, J. Chem. Phys. 2, 713 (1934); 3, 266 (1935).
b) A. A. Frost and O. Oldenberg, J. Chem. Phys. 4, 642, 781 (1936)

- ² O. Oldenberg and F. F. Rieke, J. Chem. Phys. 6, 439 (1938).

to as (I)] by photographic photometry of absorption lines of OH produced by the thermal dissociation of water vapor. The spectrum was observed in the second order of a 21 ft. grating spectrograph. The equilibrium constant for the dissociation of H_2O into OH and H_2 was taken from the work of Bonhoeffer and Reichardt³ and of Zeise.⁴ This equilibrium constant was later redetermined by Dwyer and Oldenberg⁵ who measured, in effect, the temperature coefficient of the dissociation constant using the strength of the absorption lines of OH as a measure of the relative concentration of OH. They found the dissociation energy for the process $\text{H}_2\text{O} \longrightarrow \text{H} + \text{OH}$ to be 118.2 ± 0.7 k cal, a value some 3 k cal higher than that found by Bonhoeffer and Reichardt. The first calculations of the transition probability² were therefore in error since the OH concentration calculated from the data of Bonhoeffer and Reichardt was too large by a factor of 4.2; the f-values were too small by the same factor.⁵

The absolute intensities were also measured by Avramenko and Kondratjew⁶ who used as an absorption "background" the narrow emission lines of OH excited in an electric discharge. The change in intensity of these lines on passing through a furnace containing water vapor can be observed with a low resolution instrument and will give a measure of the peak intensity of the absorption lines. If assumptions are made about

³ K. F. Bonhoeffer and H. Reichardt, Z. physik Chem. A **139**, 75 (1928).

⁴ H. Zeise, Z. Electrochem. **43**, 704 (1937).

⁵ R. J. Dwyer and O. Oldenberg, J. Chem. Phys. **12**, 351 (1944).

⁶ L. Avramenko and V. Kondratjew, Acta Physicochim. USSR **8**, 567 (1937).

the widths of the absorption lines and of the emission lines used for the background, then the absolute intensity of the absorption lines can be calculated. Oldenberg and Rieke⁷ showed that the assumptions used by Avramenko and Kondratjew were quite invalid. Using their own data on the apparent line-width of OH in the furnace, they recalculated Avramenko and Kondratjew's results and obtained f-values which were about 40% larger than the values found by their own direct method. These data have also been recalculated, using different assumptions about the line-widths, by Edse.⁸ Unfortunately, the true half-width of OH is not known and consequently data obtained by using an emission line as background cannot be interpreted quantitatively.

The absolute f-values may be in error for two independent reasons: (a) erroneous measurements of the intensities of the absorption lines, and (b) errors in the calculation of the OH concentration produced by the use of incorrect thermochemical data. The present work has been confined to a redetermination of the intensities of the lines; the thermochemical data of Dwyer and Oldenberg have been used in calculating the f-values.

The f-value of OH is currently of interest in connection with the measurement of rotational population temperatures of OH in flames. Penner⁹ has shown, using the f-values given in (I), that

⁷ O. Oldenberg and F. F. Rieke, J. Chem. Phys. 6, 779 (1937).

⁸ R. Edse, Symposium on Combustion, Flames and Explosion Phenomena. Wisconsin, 1949 (Williams Wilkins Company), p. 611.

⁹ S. S. Penner, J. Chem. Phys. 20, 507 (1952); 21, 31 (1953).

for many flames self-absorption may be expected to produce erroneous temperatures. The extent to which self-absorption falsifies rotational temperature measurements in flames has, however, been debated (Gaydon and Wolfhard,¹⁰ Broida¹¹). In this connection it is of interest to note that, if the currently accepted f -value for OH were too large by an order of magnitude, then errors in temperature measurements due to self-absorption will always be very small; and, conversely, if the currently accepted f -value were too small by an order of magnitude, errors due to self-absorption will always be large. Although the work of Oldenberg and Rieke was carried out with great care and skill, the measurement of absolute intensities is often subject to large systematic errors. The present study was therefore undertaken in order to check their original determination. An f -value about one-half as large as that found in (I) was obtained in the present study. Analysis of the data shows that this establishes a lower limit to the true f -value and, further, that the uncertainties in these experiments are such that the true intensity could be greater even than the value found in (I).

II. Theory for the Determination of f -Values.

If a beam of light of frequency ν traverses an absorbing medium, then the relation between the incident and emergent light intensities,

¹⁰ A. G. Gaydon and H. G. Wolfhard, "Flames, Their Structure, Radiation and Temperature" (Chapman and Hall, Ltd., 1953) p. 249.

¹¹ H. P. Broida, J. Chem. Phys. 21, 1165 (1953).

I_0^0 and I_0 is given by Beer's law, viz., $I_0 = I_0^0 \exp(-k_\nu Nl)$, where N is the number of atoms/cc, l is the path length and k_ν is the spectral absorption coefficient. For a given spectral line which is associated with a transition between an upper state n and a lower state m ,¹²

$$\int k_\nu d\nu = (\pi e^2 / \mu c) N f^{nm},$$

where the integration is carried out over the whole width of the line, e and μ being, respectively, the charge and mass of the electron, c the velocity of light, and f^{nm} the oscillator strength or f -value for the transition. The f -value is related to the matrix element of the transition R^{nm} by¹³ $f^{nm} = \left[8\pi^2 \mu c \nu_{nm} / 3 h e^2 \right] \left[R^{nm} \right]^2$.

The f -value of a line in a molecular spectrum is therefore proportional to $\left[R^{nm} \right]^2$ which is the product of three terms representing, respectively, the electronic transition probability, the vibrational transition probability, and the rotational transition probability.

Quantities proportional to rotational transition probabilities are the rotational line strengths S_J .^{*} The numerical values of S_J for the $^2\Sigma - ^2\Pi$ transition of OH are tabulated by Dieke and Crosswhite¹⁴ who use the symbol A_K^+ for this quantity. As the rotational levels are $(2J + 1)$ fold degenerate, the contribution of the rotational transition

¹² A. C. G. Mitchell and M. W. Zemansky, "Resonance Radiation and Excited Atoms" (Cambridge University Press, 1934), p. 99.

¹³ G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules" (D. Van Nostrand Company, Inc., 1950), p. 383.

¹⁴ G. H. Dieke and H. M. Crosswhite, "The Ultraviolet Bands of OH", Bumblebee Report No. 87, Nov. 1948.

* Ref. 13, p. 127, Eq. (III-173).

† The nomenclature used in this paper for the spectral lines is that of Oldenberg and Rieke, who use the J numbering.

probability to the f -value is proportional to $S_J/(2J+1)$.^{*} Assuming ν_{mn} to be effectively a constant, as it is in these measurements, the f -values of rotational lines with lower level J'' are given by the relation

$$f_J^{nm} = F \left[S_J / (2J'' + 1) \right], \quad (1)$$

where F is a constant.

In order to measure the f -value by evaluating $\int \ln(I_0^o / I) d\nu$ directly, the absorption lines must be observed with spectral resolution such that the half width of the line is appreciably greater than the effective slit width of the instrument. If a line is observed with an instrument with insufficient resolving power, which is almost always the case, the observed intensity is too low, the error being greatest for the stronger lines. Techniques for correcting the observed values have been worked out in great detail in connection with the absolute measurement of the intensities of infra-red bands.¹⁵ The basic theorem is that the experimental values of $\int \ln(I_0^o / I) d\nu = \alpha$ approach the true value α' for lines which are weak and broad compared with the effective slit width. In the present case the intensities of several absorption lines are measured. These intensities are proportional to the rotational transition probability and frequency of the line and the Boltzmann factor for the lower level. As the frequency is, in these experiments, effectively a constant, the intensities are proportional to $\rho = S_J(\exp -E_J/kT)$.

¹⁵

- See (a) D. C. Bourgin, Phys. Rev. 29, 794 (1927)
- (b) E. B. Wilson, Jr. and A. J. Wells, J. Chem. Phys. 14, 578 (1946)
- (c) A. Thorndike, A. J. Wells and E. B. Wilson, Jr., J. Chem. Phys. 15, 157 (1947)
- (d) J. R. Nielsen, J. Thornton and E. B. Dale, Rev. Mod. Phys. 16, 307 (1944).

* Ref. 13, p. 21, Eq. (I-55).

The true intensities are obtained by evaluating $\lim_{\beta \rightarrow 0} \alpha/\beta = \alpha_0/\beta$, which is the limiting slope, when $\beta = 0$, of a plot of α vs β . This limit may be evaluated by plotting values of α/β and extrapolating to $\beta = 0$. It should be noted that this extrapolation is not necessarily linear, as was found in (I), but may show marked positive or negative curvature. Examples of the possible forms of this extrapolation are to be found in the papers by Schatz and Hornig.¹⁶ The low values of α will show considerable scatter which is exaggerated to such a degree when experimental values of α/β are plotted directly, that the probable curvature of the plot of α/β vs β may be obscured. The probable curvature of this plot can be more readily seen by carrying out the following procedure. Draw a smooth curve through the experimental points in a plot of α vs β . From the smooth curve take values of α/β , plot these against β and extrapolate to $\beta = 0$. This procedure does no more than evaluate the limiting slope of the smooth curve. The values quoted in the present work were obtained by this method; the limits of uncertainty quoted take cognizance of the fact that the true limiting slope is poorly defined.

An alternative method of determining the f-value is to measure the "Total Absorption" $A' = \int [(I_v^0 - I_v)/I_v^0] dv$ which is, in principle, independent of the instrumental resolving power. This method is described by Minnaert¹⁷ and has been used extensively by A. S. King, R. B. King and their collaborators^{18, 19} in measuring the f-values of atomic lines.

¹⁶ P. N. Schatz and D. F. Hornig, J. Chem. Phys. 21, 1516 (1953).

¹⁷ M. Minnaert, "The Observatory" 57, 328 (1934).

¹⁸ R. B. and A. S. King, Astrophys. J. 92, 377 (1935); 87, 24 (1938).

¹⁹ R. B. King and D. C. Stockbarger, Astrophys. J. 91, 488 (1940).

A plot of the "Total Absorption" for a set of lines in an absorption spectrum vs log (number of absorbing atoms x appropriate f-value) is termed a curve of growth. Absolute curves of growth have been calculated by Schütz,²⁰ van der Held,²¹ and by Penner and Kavanagh²² for various line shapes and over various ranges of intensity and optical density. The line shape is described by the parameter $a = \left[(\Delta\nu_n + \Delta\nu_c) / \Delta\nu_D \right] \sqrt{\ln 2}$ where $\Delta\nu_n$, $\Delta\nu_c$ and $\Delta\nu_D$ are respectively, the natural, collision and Doppler half-widths. If $a = 0$, the line is a purely Doppler-broadened line with negligibly small natural line-width. In the absolute curves of growth the quantity $(A' / \Delta\nu_D) \sqrt{\ln 2} = A$ is plotted on a logarithmic ordinate; the quantity $\log \left[(N \ell / \pi \Delta\nu_D) \sqrt{\ln 2} \right] = B^*$ is plotted as an abscissa, where N is the number of absorbing molecules/cc, ℓ is the path length, $A' = \int \left[(I_\nu^0 - I_\nu) / I_\nu^0 \right] d\nu$.

The procedure for the calculation of an f-value is as follows. Values of A are calculated. The number of atoms in each rotational level N_j is known; f-values are taken from Eq. (1), using an arbitrarily chosen value of F . Arbitrary values of B can therefore be calculated. A plot of A against B will give an experimental curve of growth running parallel to the absolute curve of growth which passes through the point $A = B = 0.1$. The intercept on the B axis of the experimental curve will give the factor by which the arbitrarily

²⁰ W. Schütz, Z. Astrophys. 1, 300 (1930).

²¹ E. F. M. van der Held, Z. Phys. 70, (1930).

²² S. S. Penner and R. W. Kavanagh, J. Opt. Soc. Amer. 43, 385 (1953).

* Ref. 13, p. 132.

chosen value of F has to be multiplied in order to give the true value.

III. Experimental

The absorption cell was made of Vycor tubing 50 cms long and 4/5 cms in diameter to which quartz windows were sealed. The cell was placed in the center of an electric furnace 90 cms long and 6 cms in diameter which was wound with 14 gauge nichrome V wire. Two extra windings of 19 gauge nichrome V wire were placed over the two end sections of the furnace to make the temperature gradients more uniform along the length of the cell. Temperatures of 1300° - 1400° K could be maintained with a total power input of about 2 k.w. The power input was raised to about 3 k.w. during the initial heating period. The Vycor tubing devitrified, becoming quite brittle, at temperatures of about 1450° K, at which temperature the quartz windows fairly rapidly lost their transparency, becoming noticeably etched. The useful life of a cell at this temperature was only a few hours; long enough for one or two runs. At temperatures some 80° lower the cells could be used without difficulty for a prolonged series of runs. Temperatures were measured with a Pt-PtRh thermocouple in a probe which could be moved along the furnace, the probe lying between the absorption tube and the furnace core. In control experiments it was shown that, under the experimental conditions, this was an accurate measure of the temperature of the gas in the cell. Temperature variations along the length of the cell were ordinarily 10 to 15° . Temperatures were taken at frequent intervals during a run. After about six hours running the temperature of the furnace was sensibly constant for periods of an hour or more.

Oldenberg and Rieke did not use an absorption cell as wide bore hard

glass or quartz tube was not then available. The mixture of water vapor and oxygen was contained in a tube of "Pythagoras" composition 110 cms long, the central 50 cms of which was electrically heated. They measured the temperature distribution along the whole tube and calculated the total amount of OH present by a graphical integration. The fact that their absorbing path was not sharply defined, as by a window, but only by the temperature gradients in the furnace, is a possible source of error.

A mixture of oxygen and water vapor ($1/3 \text{ O}_2$, $2/3 \text{ H}_2\text{O}$) was obtained by bubbling oxygen through distilled water in a thermostat maintained at 89.6°C . The mixture was led into the absorption tube via an electrically heated lead tube. Saturation was ensured by using two bubblers in a series. The composition was satisfactorily checked in control experiments. Further, the change in the strength of the lines observed when the thermostat temperature was lowered, thus changing the composition of the mixture, was in accord with the predicted change.

The absorption spectra were observed in the third order of Dr. R. M. Badger's Eagle-mounted 21 ft. grating spectrograph. The light source was a 150 watt Hanovia high pressure xenon arc which gave a very good continuum in this region. A Corning 9-54 filter was used to remove light in the second order. A suitable density was obtained with exposures of about an hour, on Eastman IV-0 Plates. * Exposures were

* In Oldenberg and Rieke's experiments a hydrogen discharge tube was used as light source with a cylindrical lens in front of the plate. Only a short length of the spectrum and, consequently, only a few lines could be observed. Several of their stronger lines were blended with quite strong satellites. The contours of the "unblended" lines were separated semi-empirically from those of blended lines. In this study the whole band could be observed and, consequently, lines could be selected for photometry which were quite free from overlapping.

longer if the cell had been in use for some time and the windows had become etched.

A 4 x 10" plate was cut in two, one half being used in the grating spectrograph and the other being used for calibration. The two plates were developed together with continuous brushing. In the range of slit widths used for the microphotometer (equivalent to the slit width of the spectrograph or less by a factor of 4) the apparent areas and peak intensities of the lines were constant. Areas under the lines were estimated graphically. For the weaker lines it was sufficiently accurate to use a triangular line profile, a procedure which simplified the calculations considerably.^{18, 19}

IV. Calculation of the OH Concentration

The calculation of the concentration of OH followed exactly the procedure followed in (I), but used the equilibrium constants given by Dwyer and Oldenberg.⁵ The relationship used is that

$$(K_{OH})^2 / K_{O_2} = (P_{OH})^4 / (P_{H_2O})^2 P_{O_2} \quad \text{where } P_{OH}, P_{H_2O}, P_{O_2}$$

are the partial pressures of hydroxyl, water vapor and oxygen, respectively, and K_{OH} and K_{O_2} are the constants for the equilibria $4OH \rightleftharpoons 2H_2O + O_2$ and $2H_2 + O_2 \rightleftharpoons 2H_2O$, respectively. Suitable corrections were made for temperature variations in the cell. These were always small.

The numbers of radicals in each rotational level were derived from the partition function which was calculated using the energy levels tabulated by Dieke and Crosswhite. In this calculation it should be noted that while each energy level is doubly degenerate because of Λ doubling, each line arises from only one of the Λ components.

The absolute f-value is very sensitive to the value of the equilibrium constants. According to Edse⁸ the best available value of K_{OH} is that

of Dwyer and Oldenberg, but the uncertainty in the value is still large and would correspond to an uncertainty in the absolute f -value of at least a factor of two.

V. Results Obtained by Oldenberg and Rieke

The instrument used in (I) had a theoretical resolving power of 0.145 cm^{-1} and in other experiments this limiting resolution was quite closely approached. The absorption lines of OH had an apparent half-width of 0.58 cm^{-1} . If this is taken as the true half-width then there would appear to be sufficient resolving power to evaluate $\int L(I_y^0/I_y) dv$. The relative strengths of the lines were not, however, in the ratios predicted by theory. Instead of being a constant, the value of α/β , (using the notation of Section 2) for the strongest lines was about half that for the weaker lines. The plot of α/β vs β was apparently linear. The final value which they obtained, recalculated using Dwyer and Oldenberg's equilibrium constants and redefined through Eq. (I), is $f = 3.17 \times 10^{-4} S_J / (2J + 1)$. They estimated that the overall uncertainty in their f -value was $\pm 15\%$.

From the data given in (I) it is possible to derive, for each line, values of A and B, the parameters used in plotting the curve of growth. Oldenberg and Rieke found that all their line profiles were similar to that of the $Q_1(6 \frac{1}{2})$ line. From their published line contour it is possible to construct a plot of $(I_y^0 - I_y)/I_y^0$ as a function of v and to construct curves (a) relating $\int L(I_y^0/I_y) dv$ with the peak intensity of the line, (b) relating $\int \left[(I_y^0 - I_y)/I_y^0 \right] dv$ with the peak intensity. It is then possible to derive values of $\int \left[(I_y^0 - I_y)/I_y^0 \right] dv$ from the data given in (I) and hence values of A for the lines they measured. These values of A are plotted in Figure 1 against the appropriate values of B

using the concentrations calculated from Dwyer and Oldenberg's values of the equilibrium constants, and a value of $F = 3.17 \times 10^{-4}$ [Eq. (1)]. The theoretical curves of growth for $a = 0$ and $a = 0.5$ have been drawn on the same graph. It can be seen that it is possible to vary the value of F over quite a wide range ($\pm 20\%$) and still obtain a reasonable fit to the curve of growth. As B is a logarithmic function this is equivalent to shifting all the points \parallel to the B axis. There is a distinct trend for the stronger lines to fall on the curve of growth with $a = 0$. This trend, which is also observed in the present study, is difficult to understand. The amount of collision broadening in OH is, at the moment, a matter for speculation but it can hardly be negligible.

VI. Results of the Present Study

Runs were made at temperatures between 1360°K and 1460°K with mixture composition ranging from the optimum 66% H_2O , 34% C_2 , to 5% H_2O , 95% O_2 . The data from 5 runs were evaluated completely and were found to give consistent results. Figures 2 to 5 are specimen plots of two runs showing the method of calculation via α . The curves drawn in Figs. 4 and 5 were obtained from the smooth curves drawn in Figs. 2 and 3. They indicate the probable upward trend in values of α/β as $\beta \rightarrow 0$. Figures 6 and 7 show the results plotted as curve of growth.

The mean f -values derived, defined by Eq. (1), are:

$$\text{extrapolation method} \quad f = 1.60 \times 10^{-4} S_j / (2J + 1);$$

$$\text{curve of growth method} \quad f = 1.45 \times 10^{-4} S_j / (2J + 1).$$

The higher value given by the extrapolation method is due to the greater importance of the intensities of the weaker lines in defining the form of the extrapolation. The uncertainties in both these values are $\pm 20\%$ due,

in the first case, to uncertainties in the precise form of the extrapolation and, in the second, to the flexibility of "fit" of the curve of growth. The best fits are for a curve with $a = 0$.

It should be borne in mind that the measurement of these intensities is quite inaccurate; for weaker lines, which comprise most of those measured, the uncertainty is $\pm 15\%$ or more. This uncertainty comes mainly in the position of the "background" intensity on the microphotometer trace.

VII. Discussion

Large errors in absolute intensity measurements can be caused by lack of resolution. In both Oldenberg and Rieke's work and in the present study the effective resolution is far from ideal, as is shown by the fact that the strongest lines had only about $1/2$ of their "true" intensity.

The resolving power of the present instrument was apparently somewhat less than that used in (1) in that the absorption lines were wider with a half-width of 0.86 cm^{-1} as against 0.58 cm^{-1} . The performance of the grating with emission spectra would not lead one to suspect that it would be inferior to the performance of the grating used by Oldenberg and Rieke. We are comparing here two different criteria of resolution. The first, the Rayleigh criterion, gives the minimum resolvable separation between two lines. The absolute intensities and contours of these lines will probably be distorted. The criterion required in this work, where absolute intensities are being measured, could be defined in terms of the half-width of the narrowest line whose contour will be observed without appreciable distortion. It can be seen that the latter criterion is more stringent than the Rayleigh criterion.

Slater ²³ has given a method by which distortions to the true line contour caused by using an instrument of finite resolving power can be eliminated and the true line contour derived from the observed contour. Oldenberg and Rieke used this correction. Assuming that their instrument would resolve 0.145 cm^{-1} , and making an allowance for the distortions in the microphotometer, they found that these corrections were small, of the order of a few percent, nowhere near the factor of 2 which is required. It follows, therefore, that the effective resolving power for estimating absolute intensities is much less than they had assumed and that the "effective" slit width is much greater than 0.145 cm^{-1} . These conclusions apply also to the present work.

The effective slit width required to double the intensity of the line is large and would be greater than the apparent half-width of the line. Slater's method of correction would not be valid in such a case. The cause of this instrumental distortion is, at the moment, obscure.* It is so large that one can seriously question whether any of the estimates of line intensity are valid. In making the correction for lack of resolution the values of α/β only approach the true limit as $\beta \rightarrow 0$ for weak lines which are broad compared with the effective slit width. As the true line contour and half-breadth cannot be given, even approximately, by the observed contour, we do not know that the true limiting value of α/β

²³ J. C. Slater, Phys. Rev. 25, 783 (1925).

* To quote Oldenberg and Rieke "...we were led to the conclusion that the overall resolving power is considerably less than we had assumed. Without extensive tests it is impossible to decide if the discrepancy lies in the grating, the densitometer or the inability of the photographic plate to reproduce accurately steep intensity gradients."

is being measured. All that can be said is that the absolute intensities obtained in this manner define a lower limit to the true value.

The curve of growth method is, in principle, independent of the resolving power although estimates of the "total absorption" will become less accurate as the resolution is decreased for, as the apparent peak intensity is lowered, some intensity will be "lost" in the wings of the line. The method should be applicable to the present case with, however, some reservations. The assumption that the lines in a band will lie on one curve of growth is equivalent to saying that they are all collision-broadened to the same extent or, more simply, that they all have the same shape. It is, however, quite reasonable to suppose that, for the lines in a band, collision broadening is a function of J ; consequently, each line will lie on a slightly different curve of growth. In the region of the curve of growth which we are using, the results of such an effect may be expected to be small but the possibility must not be overlooked.

This consideration and the large experimental scatter makes the use of the curve of growth, in this case, somewhat uncertain. It has been already noted that there is a distinct trend for points from stronger lines to lie near the curve for $a = 0$. As the amount of collision broadening in OH can hardly be negligible, this makes one suspect again that there is some systematic error in measuring the relative and/or absolute intensities of the lines, or, perhaps, that the line shape is not constant. It does, however, seem that the true half-width may be appreciably less than the observed half-width.

After a critical study of the present experiments it was concluded that the temperature and composition of the gas in the furnace and the apparent intensities of the lines were as well defined as in the work of

Oldenberg and Rieke. As an absorption cell was used, the path length is better defined and the corrections for temperature gradients are smaller than in their work. It is, however, well-known that systematic errors and lack of sufficient resolving power in absolute intensity determinations almost invariably lead to low values. The result of the present work, when compared to the higher f -value obtained by Oldenberg and Rieke, is accordingly suspect. These results do, however, show that the order of magnitude of the f -value is correct and establish a lower limit to the true value. This is apart from the uncertainties in the thermal data on the dissociation of H_2O .

The considerable uncertainties in the photometric measurements make it difficult to estimate how far the lower limit we have established differs from the true value. This true value could be even greater than that found by Oldenberg and Rieke. A prerequisite for further work on molecular f -values is a study of instrumental distortions in the measurement of intensities of absorption lines.

Acknowledgement

The author wishes to acknowledge the advice and helpful criticism given during the course of this work by Dr. S. S. Penner, who suggested this problem, and the many helpful discussions he has had with Dr. R. M. Badger who generously extended the facilities of his laboratory for this work.

CAPTIONS TO THE FIGURES

Fig. 1. A curve of growth calculated from Oldenberg and Rieke's data.
 $A = (A' / \Delta \nu_D) \sqrt{\ln 2}$. $B = \log_{10} \left[(N f \ell / \pi \Delta \nu_D) \sqrt{\ln 2} \right]$. The absolute values of B correspond to Oldenberg and Rieke's final f-values.

Fig. 2. Values of $\alpha = \int \ln(I_0/I) d\nu$ plotted against $\beta = S_J \exp(-E_J/kT)$. The temperature in this run was 1460°K.

Fig. 3. Values of α plotted vs β for a run at 1380°K.

Fig. 4. Values of α/β plotted vs β from the data plotted in Fig. 2. The curve is a plot of values of α/β vs β obtained from the smooth curve drawn in Fig. 2. This curve only indicates the probable form of the extrapolation.

Fig. 5. Values of α/β plotted vs β for the data plotted in Fig. 3. The curve was drawn as in Fig. 4.

Fig. 6. The data used in Fig. 2 plotted as a curve of growth showing the apparent "fit" of the points to curves with a ~ 0 .

Fig. 7. The data used in Fig. 3 plotted as a curve of growth showing the apparent "fit" of the points to curves with a ~ 0 .

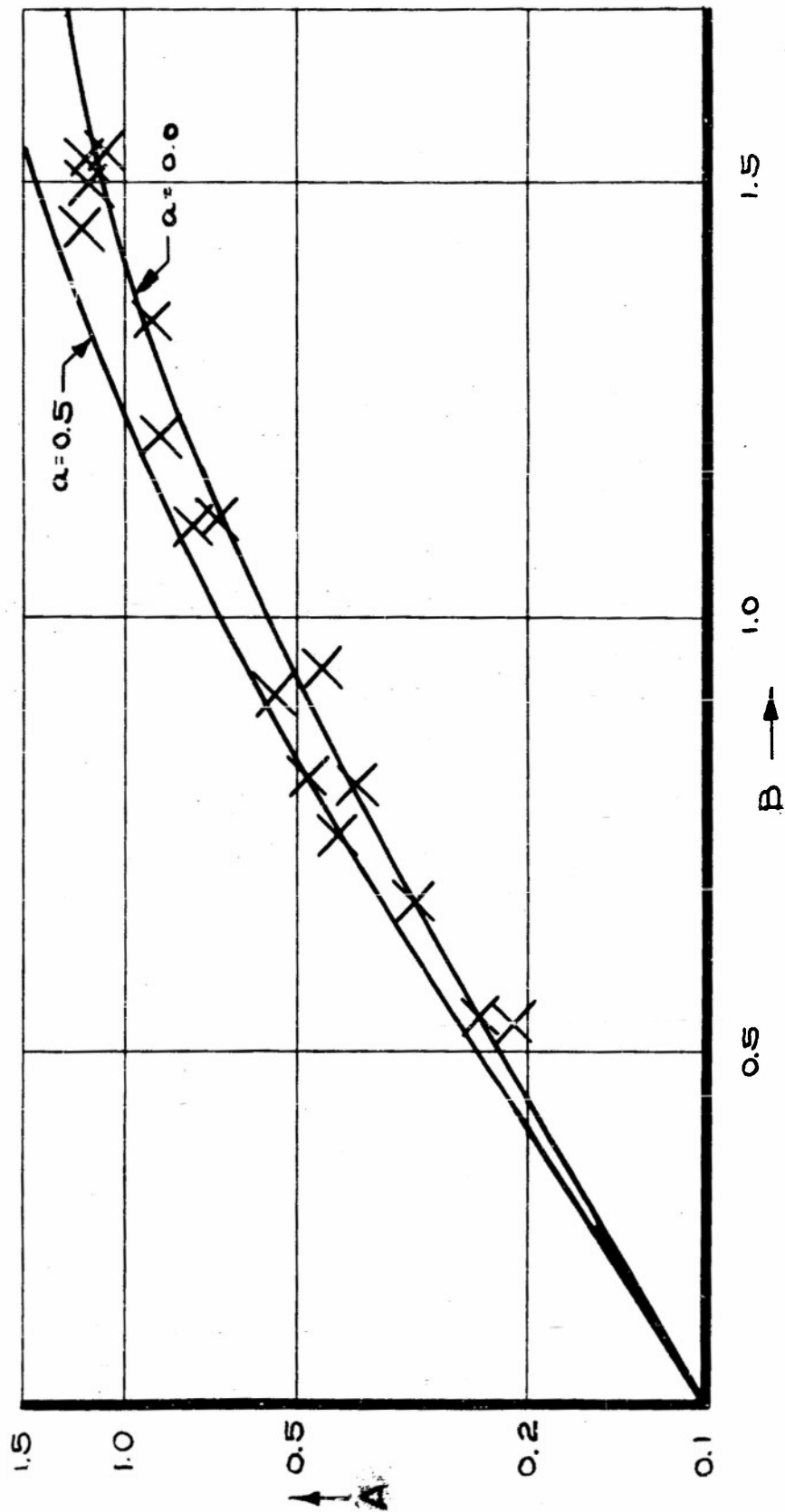


Fig. 1

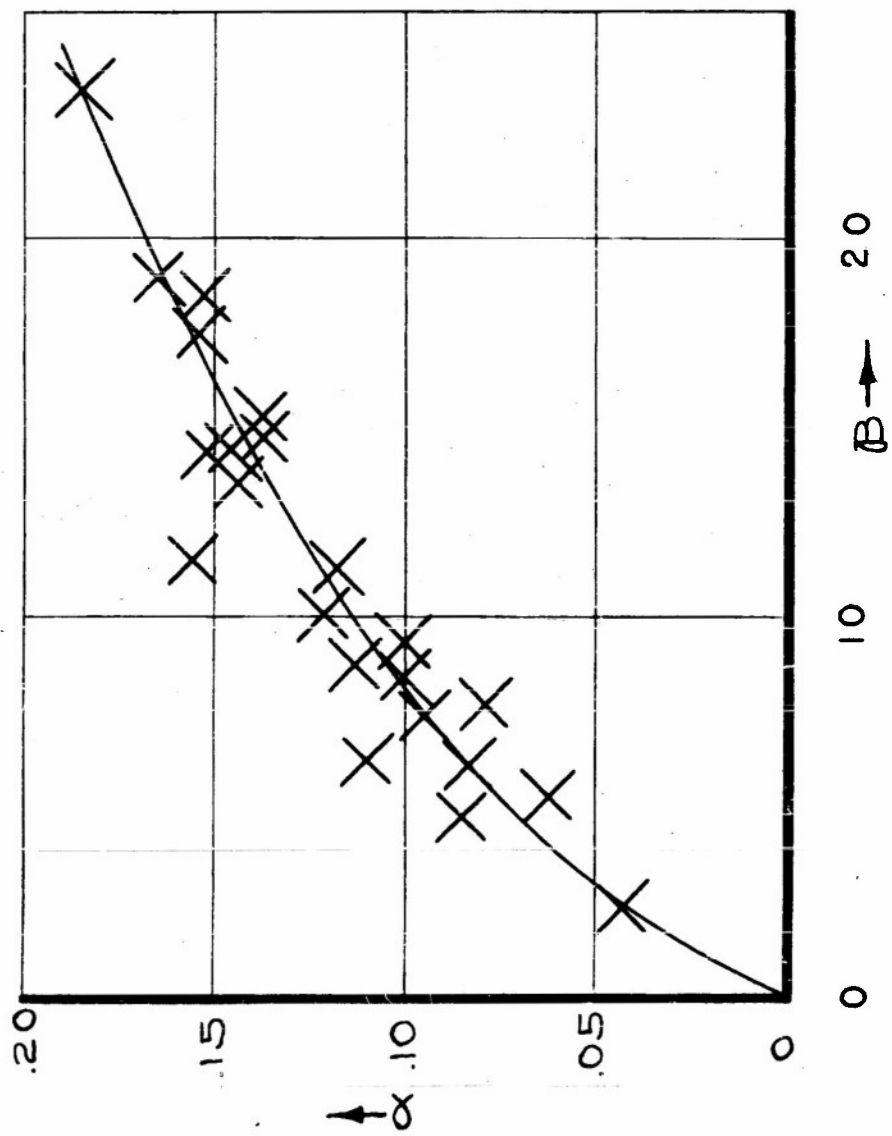


Fig. 2

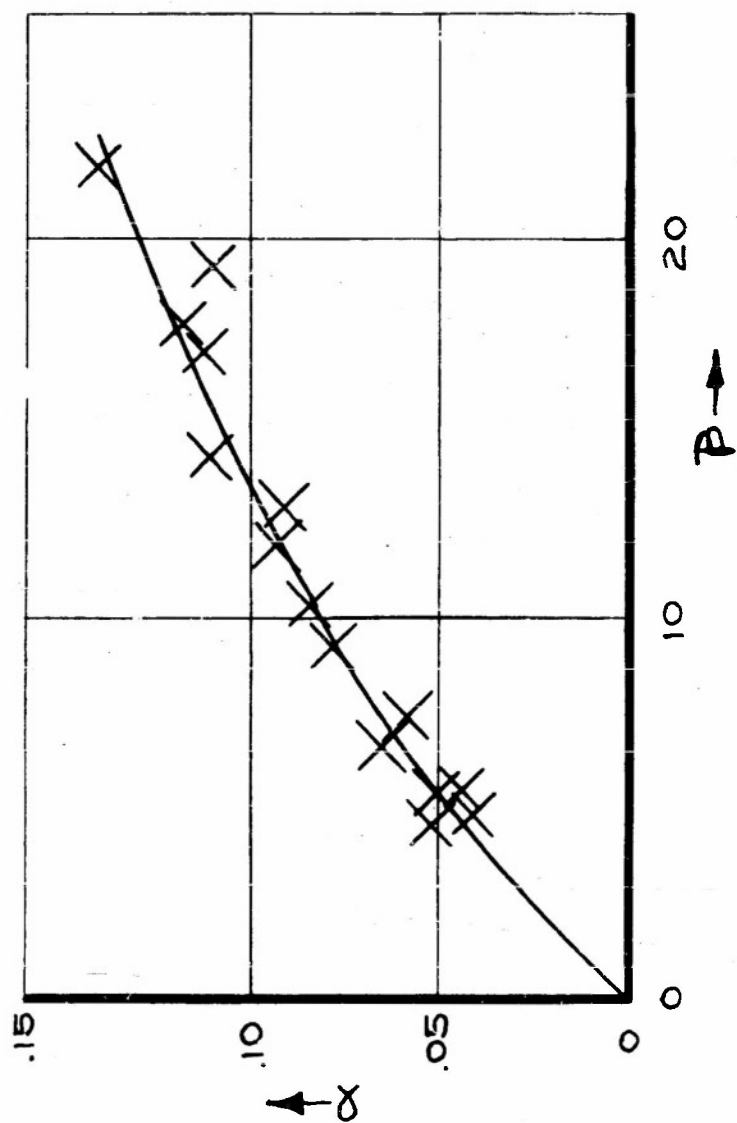


Fig. 3

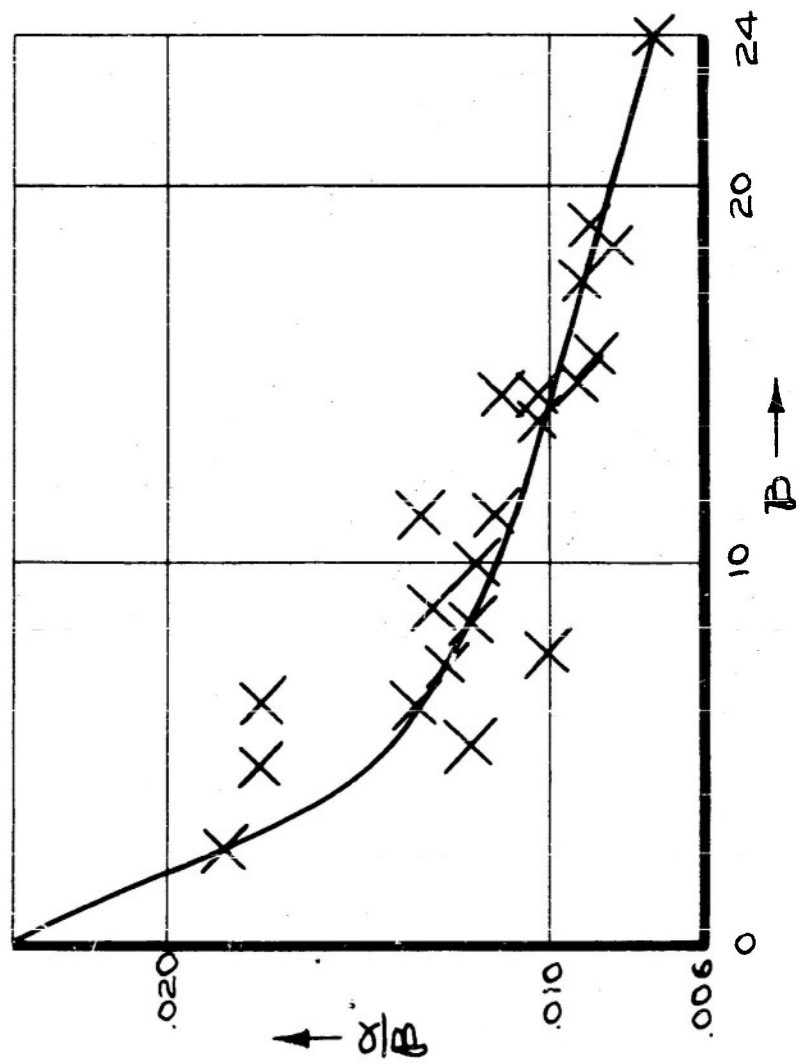


Fig. 4

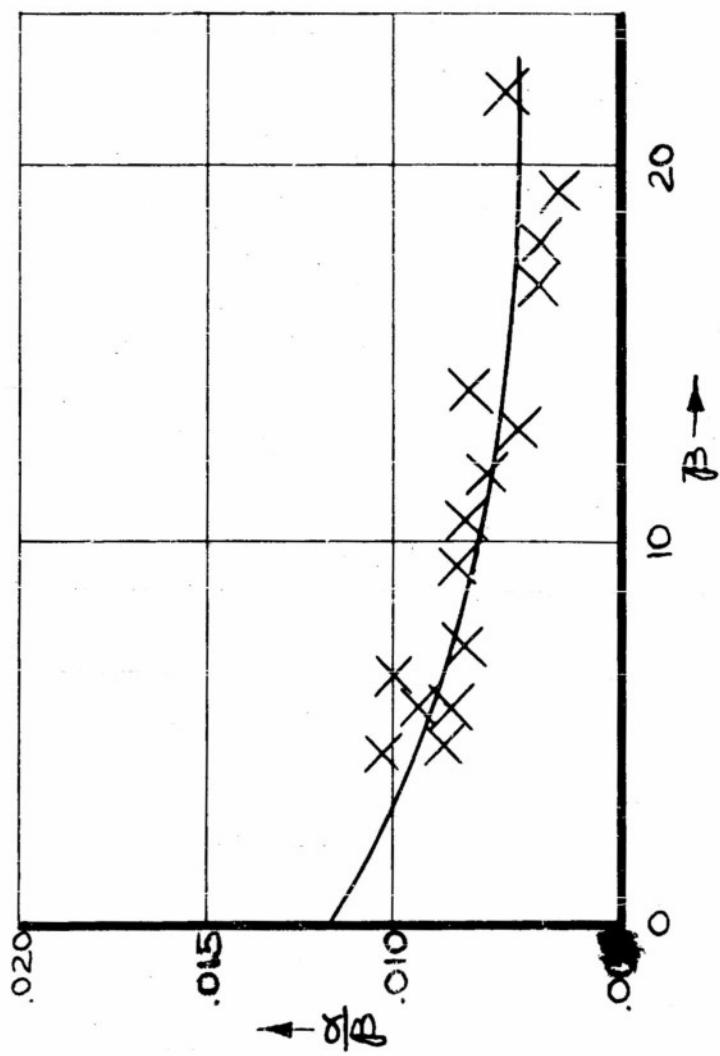


Fig. 5

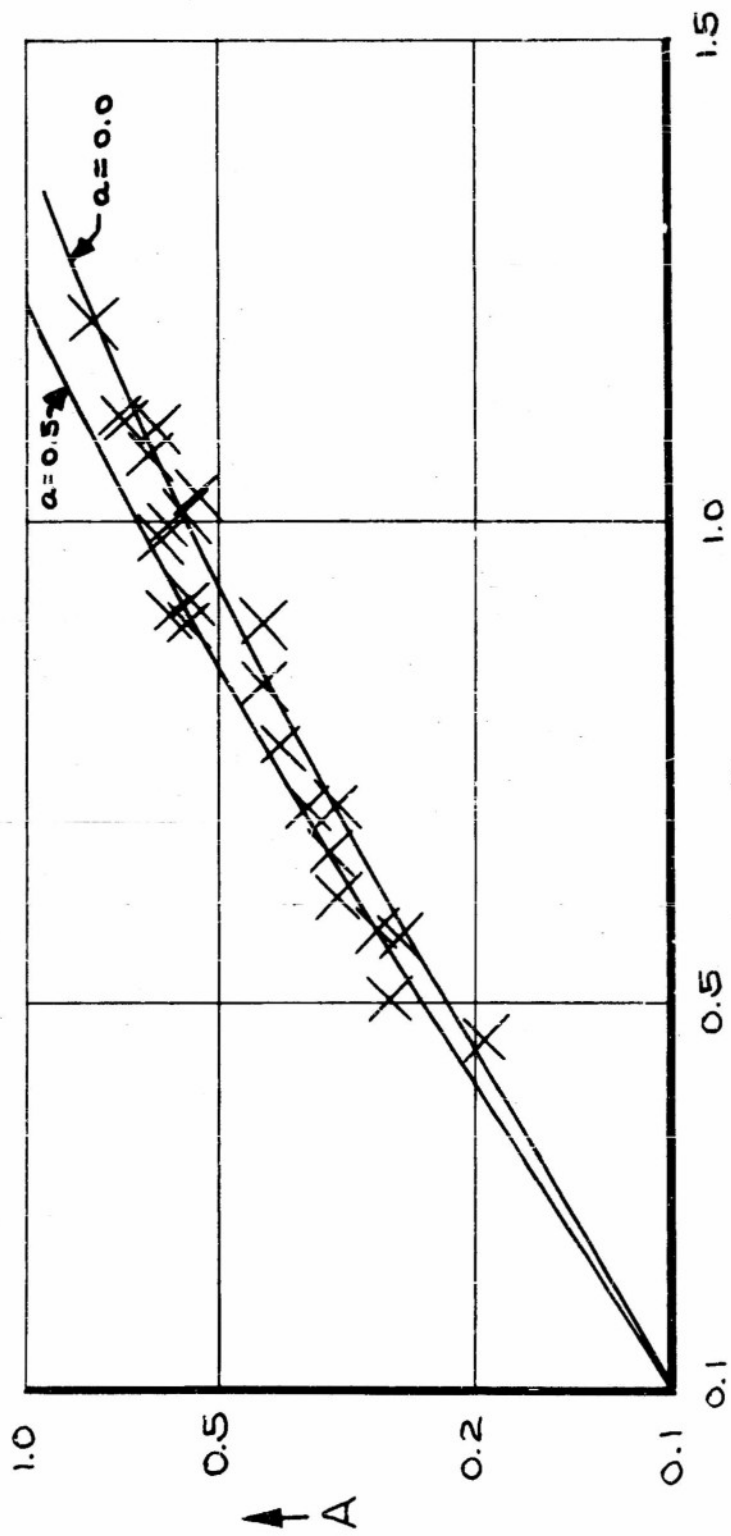


Fig. 6

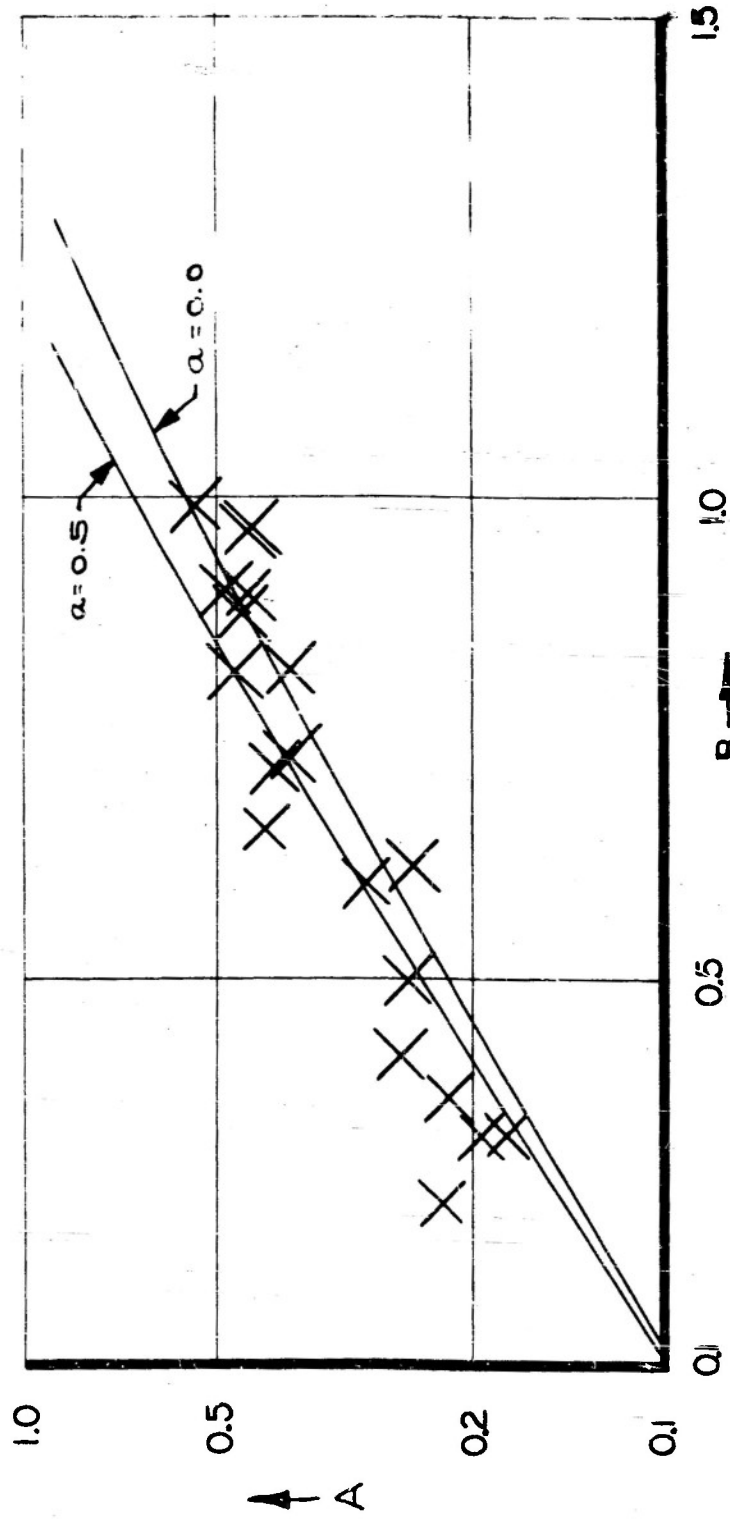


Fig. 7